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## SYNTHESIS OF TIALITE CERAMICS USING THE METHOD OF HETEROGENOUS PRECIPITATION

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The processes of synthesis of tialite ceramics using the method of heterogeneous precipitation are investigated. The effect of various factors (pH of the medium, order of precipitation, nature of the  $TiO_2$ ) on the phase transformations in the course of heat treatment is studied. It is established that this method makes it possible to obtain high-quality ceramics and at the same time decrease the synthesis temperature.

Production of a new generation of ceramic materials calls for the development of new technologies that would make it possible to manufacture high-quality materials with decreased energy consumption. The properties of ceramic materials cannot be improved significantly by using traditional methods. The reason is that material properties are determined by heterogeneities of their structure and chemical composition and the content of undesirable impurities.

In this context, researchers in all leading industrial countries are developing new methods that make it possible to produce single-fraction ceramics that are homogeneous in chemical and phase composition and structure with particle sizes below 1  $\mu m$ . These methods include homogeneous and heterogeneous chemical precipitation, the sol-gel method, pulverizing drying of salts, cryochemical and plasmachemical methods, etc. They all have their advantages and disadvantages [1].

At the beginning of the 1980s, ceramics based on aluminum titanate, or tialite,  $Al_2TiO_5$  attracted much attention from researchers. The reason for this interest is that it is possible to make heat-resistant refractory ceramics based on tialite, owing to the very low TCLE of this crystalline phase (according to various data sources, the TCLE ranges from  $+19 \times 10^{-7}$  to  $-19 \times 10^{-7} K^{-1}$ ) and a high melting temperature (1860°C). Earlier attempts to produce ceramics based on pure  $Al_2TiO_5$  failed, since the clearly expressed anisotropy of the thermal expansion of tialite crystals (according to data in [2], the expansion along the crystallographic axes  $a$ ,  $b$ , and  $c$  is, respectively,  $+118 \times 10^{-7}$ ,  $+194 \times 10^{-7}$ , and  $-26 \times 10^{-7} K^{-1}$ ) caused the development of microcracks that impaired the mechanical properties of the ceramics. The bending strength of sintered aluminum titanate is only

5–10 MPa [2]. By using special methods of synthesis and finely milled high-purity initial reactants, it became possible to obtain aluminotitanate ceramics with a bending strength of 62 MPa [3].

Moreover, the production of ceramics with stable properties based on tialite is impeded by the tendency of this material to decompose in the temperature range of 900–1300°C.

The traditional method for production of tialite ceramics is based on synthesis of stoichiometric mixtures of aluminum(III) oxide and titanium(IV) oxide and their high-temperature (around 1700–1800°C) firing together with lengthy holds at the maximum temperature. However, these conditions do not allow the production of ceramics with a homogeneous phase composition, since the material contains significant quantities of unreacted  $Al_2O_3$  and  $TiO_2$ .

It is possible to improve the quality of tialite ceramics and reduce the power consumption by using in synthesis initial components with a high degree of dispersion. The most interesting method, in our opinion, is the method of heterogeneous chemical precipitation, which does not require substantial material or power consumption.

To obtain initial powders by heterogeneous precipitation, we used a water-soluble salt of aluminum(III) and technical or plasmachemical titanium dioxide, which is not only one of the components but also a source of precipitation centers. The effect of the order of precipitation and the pH of the medium on the yield of aluminum titanate was investigated. With this aim, precipitates were obtained by direct and inverse pouring of the solutions. In the case of the direct order of precipitation, the precipitator is poured into the mixture of aluminum salt solution and  $TiO_2$ , and in the inverse order a mixture of aluminum salt solution and  $TiO_2$  is poured into the precipitator solution. The pH values of the medium varied from 6 to 8. The powder compositions and the conditions for their synthesis are given in Table 1.

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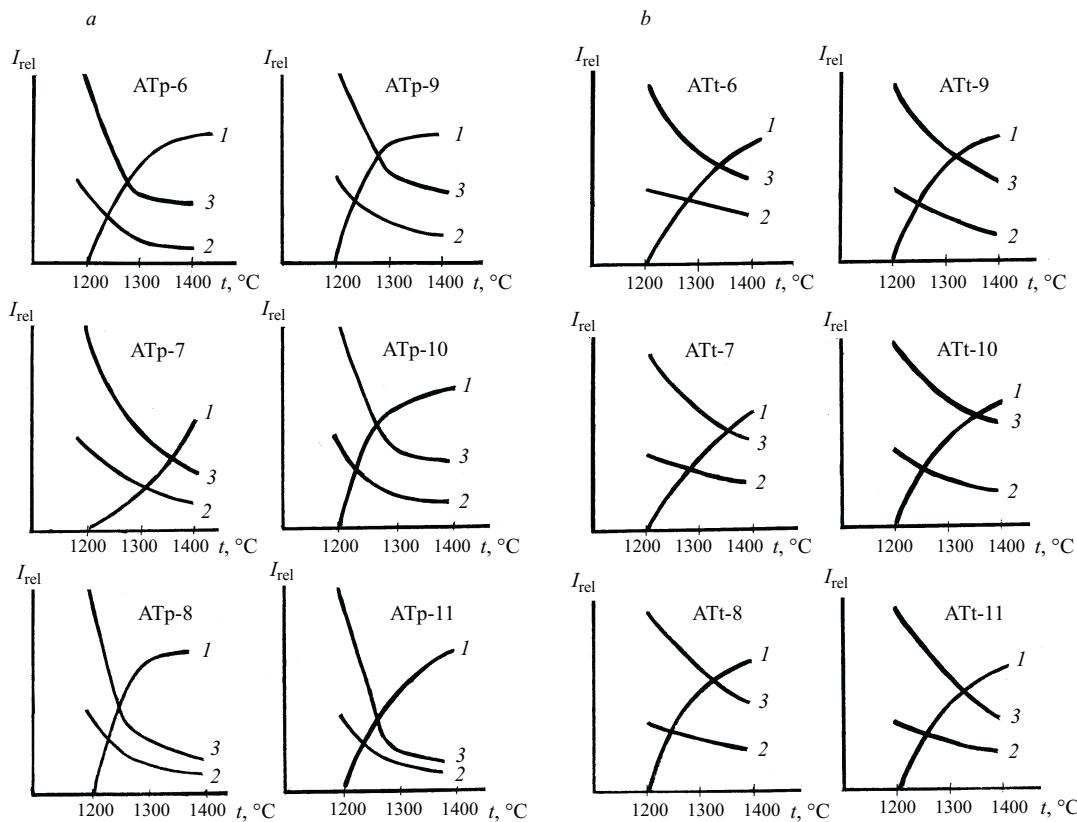


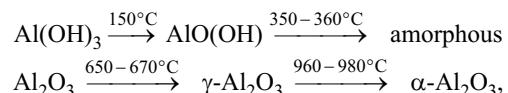
Fig. 1. Intensity of diffraction maxima of crystalline phases versus the temperature of heat treatment of powders synthesized based on plasma-chemical (a) and technical (b) titanium dioxide: 1) tialite; 2) corundum; 3) rutile.

An x-ray phase analysis of powders of technical and plasmachemical titanium dioxide points to significant differences in the phase composition of these powders. It was found that plasmachemical titanium dioxide is found mostly in the form of anatase, and technical titanium dioxide in the form of rutile. According to literature data [2], the anatase modification of  $\text{TiO}_2$  has a higher reactivity of the initial powder, compared with rutile, which facilitates mass transfer in reaction mixtures and, ultimately, increases the tialite content. At the same time, when  $\text{TiO}_2$  exists in the form of rutile, higher temperatures are required for the start of the synthesis reaction.

The particle size of the powders used also has an effect on the reaction rate. The average particle diameter of plasma-

chemical  $\text{TiO}_2$  is 60–120 nm, while that of technical  $\text{TiO}_2$  is 60–100  $\mu\text{m}$ . The increased reactivity of plasmachemical  $\text{TiO}_2$  powder is determined by both its phase composition and high dispersion. An increase in the dispersion of stoichiometric mixtures of  $\text{Al}_2\text{O}_3$  and  $\text{TiO}_2$  substantially increases the tialite yield.

Differential thermal analysis of heat-treated coprecipitated mixtures established that aluminum hydroxide is transformed under heat treatment into a metastable  $\gamma$ -modification of  $\text{Al}_2\text{O}_3$  according to the scheme



which agrees with data in [4, 5].

Formation of  $\text{Al}_2\text{O}_3$  precipitate in the form of the  $\gamma$ -modification under heat treatment also contributes to decreasing the synthesis temperature. This phenomenon, known as the Headval effect, is related to the increased reactivity of the bodies during or as a result of crystallographic transformation [6].

To determine the temperature range of aluminum titanate formation, we carried out an x-ray phase analysis of powders heat-treated in the temperature interval of 1200–1400°C with a hold at the maximum temperature for 1 h. The de-

TABLE 1

Powder*	pH	Order of precipitation
ATt-6, ATp-6	6	Direct
ATt-7, ATp-7	7	The same
ATt-8, ATp-8	8	"
ATt-9, ATp-9	6	Inverse
ATt-10, ATp-10	7	The same
ATt-11, ATp-11	8	"

\* Tt) technical titanium dioxide; Tp) plasmachemical titanium dioxide.

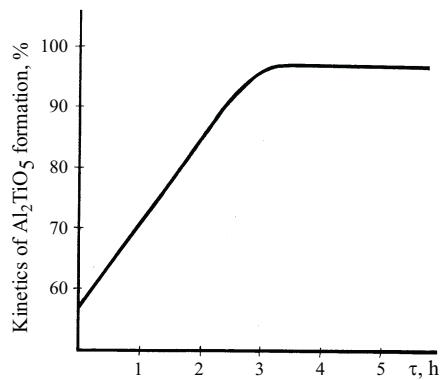


Fig. 2. Kinetics of tialite formation in the solid phase at 1450°C.

pendence of the intensity of the diffraction maxima of the crystalline phases on the heat-treatment temperature is shown in Fig. 1.

An analysis of the x-ray phase data indicates that the main increase in the amount of tialite occurs within the temperature interval of 1200 – 1300°C. According to data in [7], powders produced using the traditional method yield little tialite at 1300°C: there are only individual lines with close interplanar distances. Furthermore, it is reported in [8] that

tialite is formed only at 1400°C. Thus, increased dispersion of mixtures of  $\text{Al}_2\text{O}_3$  and  $\text{TiO}_2$  is accompanied by a substantial increase in the yield of tialite at 1300°C.

An increase in the duration of the hold from 1 to 3 h at 1400°C leads to a slow increase in the intensity of the tialite peaks and, accordingly, a decrease in the intensity of the peaks of unreacted rutile and corundum.

It can be noted that powders prepared using plasmachemical titanium dioxide have a high reactivity. Powders based on technical titanium dioxide are less active.

According to data in [9], the reaction kinetics in the solid phase at 1450°C is characterized by the curve presented in Fig. 2. This curve indicates that the reaction of tialite formation is very intense. In heating to 1450°C without a hold, over 50%  $\text{Al}_2\text{O}_3$  and  $\text{TiO}_2$  become bound. An intense course of the reaction is observed for only 2 h, and then the reaction virtually ceases, which is due to the appearance of shells of the reaction products on the initial-material grains.

For a more complete description of the processes occurring in powders based on plasmachemical  $\text{TiO}_2$  in synthesis, IR spectra of the powders obtained were recorded (Fig. 3). For identification of the spectra, absorption spectra of  $\text{Al}_2\text{O}_3$  in the form of corundum [10] and  $\text{TiO}_2$  in the form of rutile are presented as well.

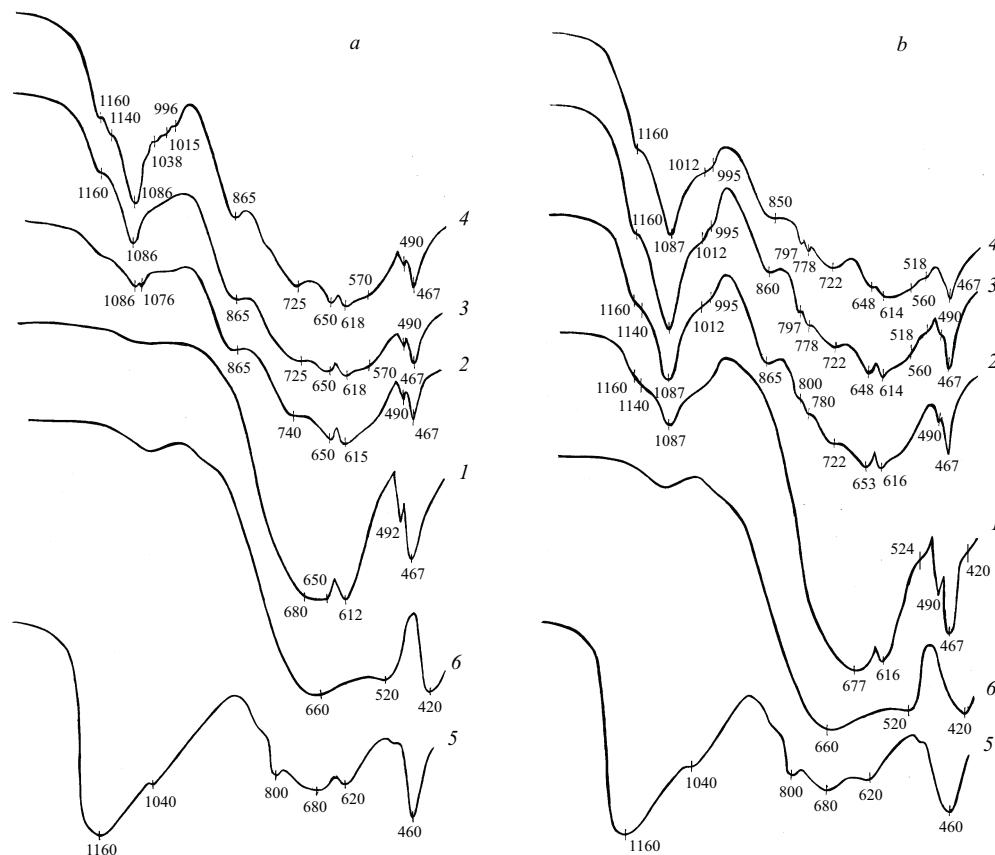


Fig. 3. IR absorption spectra of ATp-8 (a) and ATp-11 (b) powders in relation to the sintering temperature: 1) 1200°C (1-h hold); 2) 1300°C (1-h hold); 3) 1400°C (1-h hold); 4) 1400°C (2-h hold); 5 and 6) absorption spectra of corundum and rutile.

The IR spectrum of  $\alpha\text{-Al}_2\text{O}_3$  consists of a wide main absorption band in the range of  $600 - 800 \text{ cm}^{-1}$  and has the main maxima at 1160, 1040, 800, 680, 620, and  $460 \text{ cm}^{-1}$  [10]. The  $\text{TiO}_2$  spectrum is represented by a more intense main absorption band in the range of  $500 - 700 \text{ cm}^{-1}$  with the main maxima at 520 and  $420 \text{ cm}^{-1}$ . The IR spectra of powders heat-treated at  $1200^\circ\text{C}$  depend on the order of precipitation. With the direct order of precipitation (powder ATp-8), the IR spectrum is characterized by an intense main band in the range of  $600 - 700 \text{ cm}^{-1}$  with maxima at 612 and  $680 \text{ cm}^{-1}$ . The main maxima and the curve shape are similar to the rutile spectrum, i.e., the main part of titanium dioxide remains unreacted.

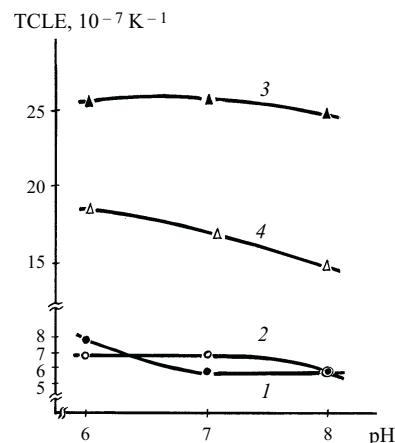
It should be noted that this spectrum does not contain absorption bands of corundum. The almost complete absence of typical corundum bands indicates that at  $1200^\circ\text{C}$  the main part of  $\text{Al}_2\text{O}_3$  exists in the form of  $\gamma\text{-Al}_2\text{O}_3$ , and not in the form of corundum. At the same time, the IR spectrum of powder produced by the inverse order of precipitation (ATp-11) consists of an intense band in the range of  $500 - 700 \text{ cm}^{-1}$  that is typical of rutile and a weak band at  $1140 - 1160 \text{ cm}^{-1}$  that points to an insignificant quantity of corundum. At temperatures  $\geq 1300^\circ\text{C}$ , the order of precipitation does not influence the shape of the IR spectral curves.

Sintering of mixtures at temperatures of  $1300$  and  $1400^\circ\text{C}$  leads to a change in the absorption bands of the powders. The IR spectra indicate the presence of a compound with a polymer structure and covalent bonds. An analysis of the IR spectra, taking into account the data of the x-ray phase analysis, indicates that these absorption spectra contain aluminum titanate, whose spectrum has a flattened profile, and its smoothness increases with increasing synthesis temperature. The deformation and stretching vibrations of the structural elements of aluminum titanate produce a continuous set of frequencies without superposition or intensification of specific frequencies. The insignificant absorption bands in the ranges typical of rutile and corundum can be evidence of their presence in extremely low quantities.

Solid-phase reactions, as distinct from reactions in liquid or gaseous media, consist of two fundamental processes: the chemical reaction itself and transfer of material toward the reaction zone. Since mass transfer is implemented by diffusion, and the diffusion mobility of the particles in a solid body depends on its structural defects [6], one can expect a substantial effect of these defects on the mechanism and kinetics of solid-phase reactions, which is actually observed in practice.

Formation of aluminum titanate is determined by mass transfer occurring in the system, which can be implemented by different mechanisms. To identify the mechanism of tialite formation, kinetic models were calculated based on known methods [6]. The calculations performed suggest that sintering of tialite ceramics proceeds via a diffusion model.

Thus, in formation of tialite, with the temperature increasing to  $1400^\circ\text{C}$ , the diffusion mechanism of mass trans-



**Fig. 4.** Dependence of the TCLE of samples on the pH of the medium and the order of precipitation: 1 and 2) samples obtained from powders based on plasmachemical  $\text{TiO}_2$  in the direct and inverse order of precipitation, respectively; 3 and 4) samples obtained from powders based on technical  $\text{TiO}_2$  in the direct and inverse order of precipitation.

fer develops. The parameters of the  $\text{Al}_2\text{O}_3$  crystal lattice are modified in sintering, and  $\text{Al}^{3+}$  ions are replaced by  $\text{Ti}^{4+}$  ions. This leads to formation of defects in the structure of the  $\text{Al}_2\text{O}_3$  crystal lattice in the form of vacancies or atoms migrating to the interstices. The stability of the defects results in an intense reaction between  $\text{Al}_2\text{O}_3$  and  $\text{TiO}_2$ . The formation of tialite spreads from the grain contact sites and boundaries to the grain centers. At a sintering temperature of  $1400^\circ\text{C}$ , the structural defects become healed, and the vacancies at the crystal lattice nodes are filled. The rate of the diffusion processes gradually becomes slower.

An important parameter of tialite ceramics is the thermal resistance of the synthesized material, which depends primarily on the TCLE determined by the phase composition of the ceramics. To determine the TCLE, ceramic rods were molded and fired at  $1400^\circ\text{C}$  with a 2-h hold at the maximum temperature.

It was found that samples based on plasmachemical  $\text{TiO}_2$  have a TCLE ranging from  $7.8 \times 10^{-7}$  to  $5.8 \times 10^{-7} \text{ K}^{-1}$ . The order of precipitation and the pH in this case do not have a substantial effect on the TCLE. In ceramics based on powders using technical  $\text{TiO}_2$ , the order of precipitation and the pH affect the TCLE. In the latter case, samples made of powders synthesized by inverse precipitation have a TCLE from  $18.8 \times 10^{-7}$  to  $14.8 \times 10^{-7} \text{ K}^{-1}$ , whereas in samples based on powders produced by direct precipitation, the TCLE is equal to  $25.8 \times 10^{-7} \text{ K}^{-1}$  (Fig. 4). An increase in the pH from 6 to 8 fosters a decrease in the TCLE.

The TCLE of ceramics synthesized on the basis of powders with plasma-chemical  $\text{TiO}_2$  is lower than the TCLE of powders based on technical  $\text{TiO}_2$ , which is also evidence of the fact that in the former case, formation of tialite is more intense, all treatment conditions being equal. This can be attributed to the fact that the determining effect on the TCLE

of tialite ceramics is produced by the microstructure, which depends on the crystal size. Using samples with different crystal sizes results in different TCLE values of tialite ceramics. Low TCLE values point to a rather complete reaction of tialite formation in powders with plasmachemical titanium dioxide, which do not depend on the pH or the order of precipitation. Weakly positive values of the TCLE in the synthesized materials point to their high thermal resistance.

Tialite obtained under optimum conditions has a TCLE of about  $6 \times 10^{-7} \text{ K}^{-1}$  and provides a tialite yield of at least 70–80%. The bending strength of such ceramics is 15–18 MPa.

The synthesized ceramics can be used as filling agents in compounds to decrease their TCLE, in heat-resistant shielding screens for induction furnaces, as high-temperature structural materials, and for engineering purposes (making tube crucibles, etc.)

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